NOTES ON DIAGRAM.

Ordinates = − log (H·). Left-hand numbers refer to upper curves, right-hand to lower.

Abscissæ = ratio alkali to acid. Upper numbers refer to upper curves, lower numbers to lower curves.

Upper Curves.

+ + and plain line—values calculated by formulæ 3*a* and 3*b* } at C = 0·1.
× × and dotted line—values calculated by formula 1 } at C = 0·1.
⊙ ⊙ Auerbach's values at C = 0·2.
+ + and broken line—values calculated by formulæ 4*a* and 4*b* { at C = 0·001 upper. at C = 0·0001 lower.

Lower Curves—Dilute carbonate on larger scale.

+ + and plain line—values at C = 0·001.
+ + and broken line—values at C = 0·0001.
⊙ ⊙ experimental values as quoted.

N.B.—The third points in Tables I and II have been erroneously plotted as 0·17 and 0·14.

Volatilisation of Extremely Thin Radioactive Deposits.

By A. B. Wood, M.Sc., Oliver Lodge Fellow and Assistant Lecturer in Physics, University of Liverpool.

(Communicated by Prof. Sir E. Rutherford, F.R.S. Received July 1, 1915.)

Introduction.

Within the last few years papers dealing with the volatilisation of radioactive substances have been published by various authors. The principal aims of the experiments described in these papers may be classified under three heads:—

(*a*) To determine the temperatures of volatilisation of the various members of the active deposits of radium, thorium, and actinium; in some cases with a view to the classification of these substances in the periodic system.

(*b*) To prove that these extremely small quantities of matter form definite chemical compounds in a manner similar to that of the commoner elements.

(*c*) To separate the various members of the series from one another.

Other interesting results, which throw light on the phenomena of volatilisation, have also been reported, but these have always formed a subsidiary part of the researches described. Makower* determined the temperatures of volatilisation of radium A, radium B, and radium C, in air, and showed that the effects observed depended to some extent on the nature of the surface on which these substances were deposited.

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* Makower, 'Manch. Lit. and Phil. Soc.,' vol. 53, Part II (1909), and 'Le Radium,' vol. 6, p. 50 (1909).

Schrader,[*] working with the active deposits of actinium and thorium, found that volatilisation commenced at a much lower temperature if the platinum wire coated with the active deposit were first exposed to an atmosphere of chlorine. He also put forward the view that, in consequence of the production of ozone by the α-particles, oxides are formed of the components of the active deposit. This explanation cleared up the mystery with regard to the great divergence between the results obtained by Russell[†] and those of Makower, previously mentioned.

Results of a similar character have also been described by Barratt and Wood,[‡] and more recently by the author.[§]

These authors have also shown the possibility of separating radioactive substances which have not yet been separated by other methods.

One feature, common to all the experiments mentioned, is the reference to possible sources of error in the determination of volatilisation temperatures. Hence it appeared to the author that an investigation of a few of the most important factors which may influence the volatilisation of these exceedingly thin films was desirable.

It is necessary, in an investigation of the nature just mentioned, to choose some substance whose behaviour when heated to various high temperatures is fairly simple. In addition to this, the behaviour of this substance must be typical of the other substances of the same character. Barratt and Wood, in studying the volatilisation of thorium B and thorium C, showed that the curve connecting the amount volatilised with temperature was quite simple in the case of thorium B, whereas the curve for thorium C was more complex. The author has also shown that the volatilisation curve for thorium D is similar to that for thorium B. We may thus reasonably assume that the volatilisation curve of thorium B is typical of that for any single constituent in the active deposits of radium, thorium, or actinium.

Consequently thorium B is the substance employed in the present experiments for an investigation of the various influences which affect the volatilisation of the active deposits.

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[*] Schrader, 'Phil. Mag.,' vol. 24, p. 125 (1912).

[†] Russell, 'Phil. Mag.,' vol. 24, p. 134 (1912).

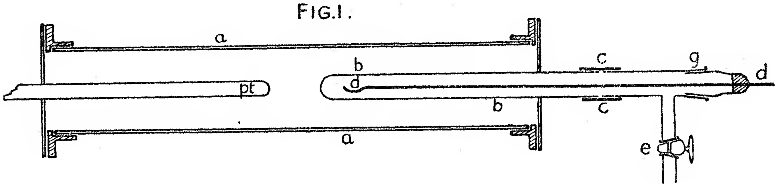
[‡] Barratt and Wood, 'Phys. Soc. Proc.,' vol. 26, pp. 248–260 (June, 1914).

[§] A. B. Wood, 'Phil. Mag.,' vol. 28, pp. 808–818 (December, 1914).

Apparatus and Experimental Procedure.

The apparatus employed is shown diagrammatically in fig. 1. An electric furnace, whose temperature could be measured accurately by means of a platinum thermometer and Callendar-Griffiths bridge, was used to heat the active material. The furnace and thermometer have been described in detail in a previous paper.*

FIG. 1.



aa. Porcelain lining of furnace. *pt.* Platinum thermometer.
bb. Fused silica tube. *dd.* Light nickel spoon.
e. Tap connecting to pump and pressure gauge.

Temperatures above 1100° C. were estimated by extrapolation of the curve connecting temperature and current through the furnace. The active substance was placed inside a tube of fused silica, closed at one end, arranged centrally in the furnace and symmetrically with regard to the platinum thermometer (see fig. 1). By means of a long nickel spoon, fixed to a ground glass joint which closed the cold end of the tube, the active material could be introduced or removed quickly from the silica tube. The nickel spoon was of very small heat capacity, and attained the temperature of the furnace in a very short time. This point is of importance, and will be referred to later (see Section 3). The silica tube was connected by means of a side tube to a vacuum pump and pressure gauge, thus making it possible to heat the active substance at any desired pressure. This arrangement also proved extremely useful in evacuating the tube between successive experiments, in order to remove any volatilised active material which would necessarily be present in the tube. A strongly emanating source of radio-thorium (equivalent in activity to 1 mgrm. of radium bromide) was used as a supply of active deposit. By a simple arrangement this could be obtained on one side only of the plate exposed to the emanation, and by varying the conditions of exposure a considerable range of activity could be obtained. In all experiments, except a few of those described in Section 2, exposures were made without electric field, a thin layer of tissue paper separating the radio-thorium from the metal foil, so that the possibility of thorium X being deposited on the foil was reduced to a minimum. The active deposit obtained in this way decayed accurately with a period of 10·6 hours, thus proving it to be free from thorium X. All measurements of activity were made by α-rays, an electroscope of the Rutherford pattern being used for this purpose.

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* A. B. Wood, *loc. cit.*

Before commencing to take activity measurements, the active deposit was allowed several hours (generally overnight) to attain equilibrium. The following procedure was adopted in the determination of the percentage of thorium B volatilised. Equilibrium having been attained, several readings of the activity were taken and the mean time of observation noted. The deposit was then placed in the nickel spoon and introduced into the furnace for the desired interval. When a period of not less than six hours had elapsed after the removal of the active deposit from the furnace, the α-activity was again measured and at the end of this time the unvolatilised portion of the deposit had again attained equilibrium.* From the observed and calculated values of the activity at the time of the second set of measurements the percentage volatilised is easily deduced. At the end of every experiment similar to the one just outlined, the silica tube was evacuated to a pressure of about 2 cm. of mercury in order to free it as far as possible from the volatilised portion of the active deposit.

Factors Influencing Volatilisation.

Earlier experiments have shown that the volatilisation of a thin film of radioactive matter varies enormously with the conditions to which it is exposed. For example, the kind of surface on which the film is deposited has a marked effect, whilst several experimenters have recorded notable variations with different gases on the furnace tube. It is unnecessary at this stage to enter into a discussion of numerous other sources of influence on this phenomenon, but the following list will serve as a guide to some of the principal factors which have been investigated in detail. The effects of variation on the following conditions have been studied:—

1. Nature of the surface on which the active substance is deposited.
2. Thickness of the layer of active material.
3. Period of heating.
4. Temperature.
5. Pressure of the surrounding gas.
6. Nature of the surrounding gas.

The first five of these factors will be considered in the order given above. The consideration of the sixth, *i.e.* the influence of the nature of the gas surrounding the active material, will be discussed in a later communication.

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* See paper by Barratt and Wood, *loc. cit.*

1. *Influence of Surface.*—Before investigating the other factors which may influence the volatilisation of the thorium B, it is necessary to choose a suitable surface as a "support" or "base" for the deposit. Barratt and Wood showed the necessity for a perfectly clean surface, since a thin film of grease, or other substance which easily volatilises, will carry away the active material with it. It is essential then to use some substance as "base" which can be cleaned easily and thoroughly, either by heating or by treatment with acids. Platinum and quartz are both ideal in these respects. It is interesting, however, to examine other substances as to their suitability. Substances whose melting points are below 1000° C. can at once be dismissed; again, all substances the volatilisation of which is detectable below this temperature are unsuitable.*

Makower† in his work on the volatilisation of radium C from surfaces of nickel, platinum, and quartz has shown that volatilisation of the active substance is appreciable in all cases between 700° and 800° C. All the radium C was driven off nickel and platinum at 1200° C. but not from the quartz till a temperature of 1300° C. was reached. Barratt and Wood, using thorium active deposit, confirmed this observation of Makower that the initial temperature of volatilisation was the same whether the active substance was deposited on quartz or platinum: but found it impossible to volatilise the whole of the deposit from either quartz or platinum even after prolonged heating at 1300° C. These conclusions are strongly supported by the results of the present experiments. It was found that after heating the active deposit on platinum for 10 minutes at a white heat (temperature estimated at 1600° C.) in the blowpipe flame there still remains an appreciable amount of thorium B unvolatilised. A similar result was obtained when quartz was used as the base. With regard to this unvolatilised portion of thorium B, the following experiment is instructive. A platinum foil coated with thorium active deposit was heated for about 60 minutes at 1200° C. and approximately 99 per cent. of the thorium B volatilised. The portion remaining on the platinum foil, *i.e.* the 1 per cent., was allowed to attain equilibrium, when it was again heated for the same time at 1200° C. It was found now that only 18 per cent. of this remaining portion of the original deposit was volatilised. These observations seem to indicate that a certain fraction of the molecules of the active deposit are held to the surface of the platinum by forces of cohesion due to the molecules of platinum in their immediate neighbourhood. Possibly this small percentage of the active deposit has penetrated below the surface molecules of the platinum by the process of radioactive recoil. Thus, when exposing the platinum plate to the emanation, an atom of thorium A on expelling an α-particle might, by its energy of recoil, travel a distance equal to the depth of several layers of molecules below the platinum surface. This recoiling atom of thorium B disintegrates (with emission of a soft β-ray) into thorium C without appreciably changing its position; then, when the atom of thorium C expels an α-particle, the recoiling atom might either penetrate still further into the platinum or make its escape again from the surface. Another possible explanation of the phenomenon is that the molecules of the active deposit and platinum conceivably intermingle near the surface on account of the energy of heat motion at these high temperatures.

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* A list of elements with their melting points, boiling points, and temperatures of initial volatilisation is given in a table in Kaye's 'X-rays.'

† Makower, 'Manch. Lit. and Phil. Soc.,' vol. 53, Part II (1909).

Recent work by Roberts* has shown that platinum, or one of its oxides, is volatilised at temperatures between 1000° C. and 1200° C., hence it is quite probable that a small portion of the active deposit is carried off by this means, in addition to the normal volatilisation.

When the active material was heated on a nickel surface, the effects observed were very conflicting. The temperature at which volatilisation commenced agreed fairly well with the temperatures noted when platinum and quartz surfaces were used. At higher temperatures, however, large divergences were sometimes observed—the results seeming to depend on the condition of the nickel surface before exposure to the emanation. Thus it was noticed that the results were more consistent when the nickel surface, before exposure to the emanation, was oxidised by heating strongly in a blowpipe flame.

The following shows the result of a series of experiments using nickel and platinum surfaces:—

(1) First Heating at 1200° C.

Surface.	Time of heating.	Percentage thorium C remaining.	Percentage thorium B remaining.
	min.		
Platinum	60	3	1
Nickel (polished)	72	8·4	3·5

After equilibrium had again been attained, the foils were reheated.

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* Roberts, 'Phil. Mag.,' 6, vol. 25, p. 270 (February, 1913).

(2) Second Heating at 1200° C.

Surface.	Time of heating.	Percentage remaining thorium C (*i.e.*, thorium C left from (1)).	Percentage remaining thorium B (*i.e.* thorium B left from (1)).
	min.		
Platinum	60	82	70
Nickel (now oxidised)	60	89	76

A third heating in the blowpipe flame (temperature between 1500° C. and 1600° C.) showed that there was a large percentage of the active deposit left from (2), still unvolatilised. It will be clear from these results that it is with only very great difficulty that the last 2 or 3 per cent. of the active deposit can be volatilised. Again, it is more difficult to remove the active deposit from nickel than from platinum. As one would expect, the nickel, on removal from the furnace at these high temperatures, is always coated with a thin film of black oxide, which renders this substance unsuitable as a base for several reasons—in particular, the complication of the α-ray measurements due to the absorption in the oxide film. Again, volatilisation of this film might introduce serious errors in the measurements. A surface of iron or steel is objectionable for similar reasons.

Using copper and brass surfaces this trouble of oxidation was still further increased, the comparatively low melting point of copper (1084° C.) being another serious objection to its use at high temperatures.

The metals osmium, iridium, and tungsten would be excellent for the purpose, since volatilisation of these elements has not been detected below 1400° C. *in vacuo*—on account of their expensive nature, however, they were not used in the investigation.

From the above considerations it is clear that platinum and quartz are the most suitable materials to employ in a research of this kind. On account of the ease with which it can be cleaned and manipulated platinum has been used as base for the active substance in all the experiments subsequently described.

2. *Density of the Deposit.*—When referring to such minute quantities of substance as the active deposits from the various radioactive emanations we cannot use strictly the term "thickness." Assuming a uniform distribution of particles, a simple calculation of the thickness of a very active layer of thorium active deposit, equivalent in γ-activity to 7·5 mgrm. of radium per square centimetre of platinum, shows that only one thousandth of the platinum surface is covered by a layer one molecule deep, *i.e.* for every

thousand surface molecules of the platinum there is only one molecule of active deposit. Hence it seems advisable to use the term "density of the deposit" where density indicates the number of molecules of active deposit per unit area of surface. It will be at once clear that this term is used in a relative sense; thus when one layer of active deposit is said to be ten times the density of another, a comparison is made between the number of molecules per square centimetre in the two cases.

It is well known that in the case of volatilisation of metals such as iron, gold, or platinum, the amount volatilised is proportional to the time of heating and to the surface area exposed. This is far from being the case, however, in the volatilisation of minute quantities of matter such as we are now considering. It will be shown later that the amount volatilised is not a linear function of the time of heating.

There are two methods open to us for varying the density of the deposit: (*a*) by varying the time of exposure to the emanation, without employing an electric field; (*b*) by exposing for different times with an electric field.

(*a*) By comparing the γ-activity of the active deposit with that of a standard source of radium, a simple calculation gives us the approximate number of active deposit molecules per square centimetre. Variations of exposure from 1 to 40 hours have been made without electric field, representing a range of density from $1{\cdot}5 \times 10^{10}$ to $1{\cdot}5 \times 10^{11}$ active deposit molecules per square centimetre—the number of platinum molecules in a surface layer being of the order 10^{16}. No regular variations in the amount volatilised with change of density of the deposit were observed, all differences being well within the experimental error. Hence, under these conditions, the volatilisation is independent of the time of exposure to the emanation.

(*b*) If an electric field is used when exposing to the emanation, the density of the deposit can be increased to about one hundred times the maximum possible by method (*a*), *i.e.* to a density of about 10^{13} molecules per square centimetre.

Now, however, fairly large and almost unaccountable variations occur. Several explanations of these variations can be suggested. They may be due (1) to the collection of charged dust particles or other nuclei, coated with active deposit, (2) to the formation of charged aggregates of active deposit, and to the non-uniformity of the layer of active deposit collected by this method, as compared with that obtained by the ordinary process of diffusion. In all cases, however, the amount volatilised from a plate exposed, till equilibrium is reached, by method (*b*) is greater for short periods of heating than that volatilised from a plate exposed by method (*a*).

This gives strong support to the view that dust particles or other nuclei coated with the active deposit have been collected on the plate by the electric field used in (*b*)—consequently, when such a plate is introduced into the furnace, the dust burns rapidly, and carries away the active deposit with it. This question will be discussed later (see Section 3). The following Table gives a comparison of a series of results obtained by the two methods just outlined :—

Time of heating.	Percentage thorium B volatilised at 795° C.		
	Platinum foil exposed to emanation *without* electric field.		Exposure to emanation *with* electric field.
	2 hours' exposure.	40 hours' exposure.	24 hours' exposure.
min.			
5	32	27	52
15	60	58	81
30	78	81	86
60	88	87	90

The above remarks must be modified, of course, when we are considering the volatilisation of the portion which remains after the platinum and active deposit have been once heated to temperatures over 1000° C.—this has been explained in Section 1. For experiments of this character the results are always the same, whatever the density of the original deposit.

It appears, then, that the most consistent results are obtained when the platinum foil is exposed to the emanation without electric field, the volatilisation in that case being practically independent of the time of exposure. In all subsequent experiments the active deposit was collected by exposure to the emanation for six hours without electric field.

3. *Variation of Period of Heating.*—A point of great importance in the study of the problem of volatilisation is to determine the rate at which the active material is removed from the surface.

The experimental procedure was as follows: After the furnace had attained a steady state (usually after about 2 hours' preliminary heating) the active deposit, previously measured, was introduced into the furnace for a definite period, by means of the nickel spoon. On removal its activity was measured as explained above. The silica tube was then evacuated to remove volatilised active deposit, and a second source of active deposit introduced for another different period. This process was repeated until a series of observations had been made giving the relation between the time of heating and the amount volatilised at a particular temperature. The temperature of the furnace was now altered to another value, and, after a steady state had again been reached, the above order of experiment repeated. It should be pointed out at this stage that the minimum time of heating in the furnace was about two minutes, on account of the small but appreciable time (perhaps 30 seconds) required by the nickel spoon to attain the furnace temperature. This difficulty was surmounted, as far as seemed possible, by lining the spoon with a thin layer of asbestos, consequently the small piece of thin platinum foil would probably reach the furnace temperature in a much shorter time than that required for the spoon.

The result of such a series of observations is shown in fig. 2.

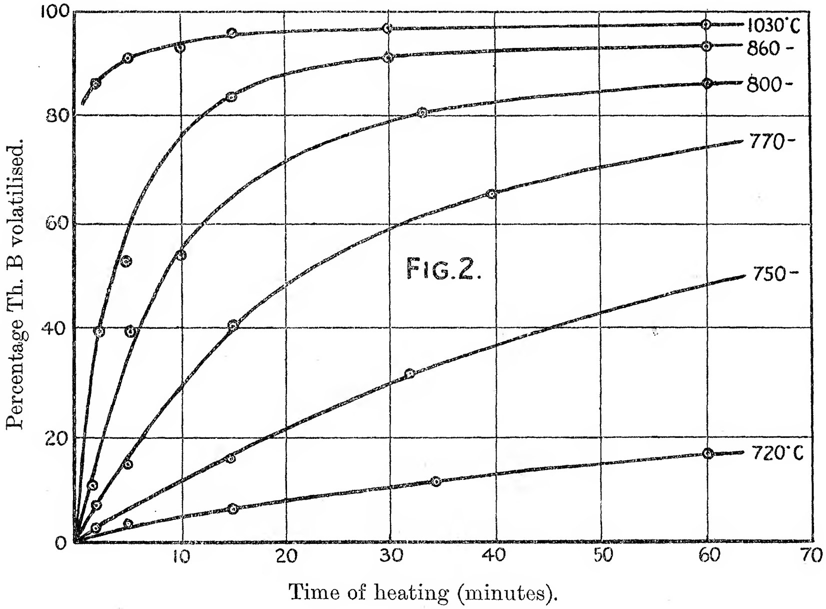

FIG. 2.

Two prominent features of these curves will be noticed at once.

(1) The amount volatilised increases at first rapidly, then more and more slowly as heating is continued, *i.e.* the rate of volatilisation decreases rapidly with time of heating, particularly at high temperatures.

(2) The initial rate of volatilisation increases very rapidly with small increases of temperature. This point is shown more clearly in fig. 4, which will be discussed in Section 4.

Another, though perhaps less important, feature of these curves will be noticed from a consideration of the rate when a large percentage has been volatilised. A decided flattening of the curves becomes evident as the amount volatilised approaches the maximum value, thus indicating that it would take an extremely long period of heating to remove the last traces of the thorium B—in fact, a similar curve (not shown in figure) at 1200° C. runs practically parallel to the time axis, with 99 per cent. as ordinate. This gives further confirmation of the results mentioned in Section 1.

The first explanation of the form of the curves which suggests itself is that they are exponential. It seems quite reasonable to suppose that the rate of volatilisation is proportional to the amount of active substance present on the platinum foil at any particular time, *i.e.* when we are dealing, as in this case, with a comparatively small number of molecules. The facts do not support this view, however, and it becomes necessary to look for some other explanation. Of course, it is quite probable that several factors are involved in the complex behaviour of the active deposit; hence a consideration of the following hypothetical case may throw some light on the problem.

Suppose we could obtain on a platinum surface a layer of active deposit of measurable thickness (say 0·001 mm.). Let us consider what happens when this layer is heated. Up to a certain critical point, *b* in fig. 3, one would expect the rate of volatilisation to be constant, *i.e.* the amount volatilised is proportional to the time of heating, but when the depth of the layer had decreased to one or two molecules the rate of volatilisation would begin to decrease, at first slowly, then more rapidly, until only those molecules of the active deposit which are intermingled with the platinum molecules are left. At this stage, *d* in fig. 3, the rate of volatilisation decreases more slowly, since the remaining molecules are subject to a different law of force—the cohesion of the platinum molecules—from that of the active deposit molecules volatilised in the earlier stages. Fig. 3 is a diagrammatic representation of the process just outlined The latter portion

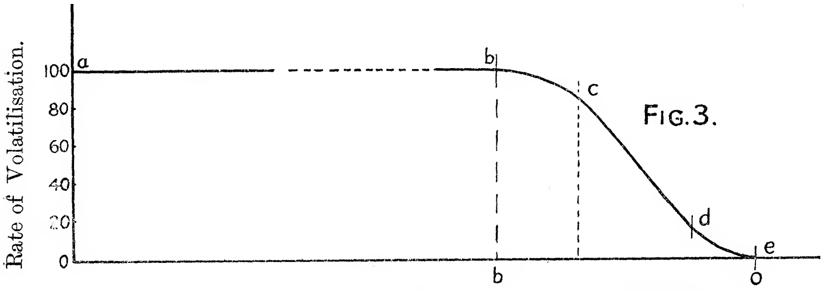

FIG. 3.

Thickness of layer (diminishing).

Maximum thickness at *a*. Infinitesimally small thickness at *b*.

Zero thickness at *e*.

of the curve, between the points *c* and *e*, represents the result of an actual experiment similar to the one described at the beginning of this section.

As was made clear in Section 2, the thickness of the active deposits is always less than that at the critical stage *b*—consequently the rate of volatilisation is never constant initially. If the above suggestions are correct we should expect, on investigating very thick layers of active deposit, to include more and more of that portion of the curve lying between the points *b* and *c*. Unfortunately, we have no sources of thorium emanation at present available, from which we can collect such thick layers of active deposit by diffusion. Owing to the disturbing action of dust particles, when an electric field is used to increase the density of the deposit, the results obtained in such cases cannot legitimately be compared with those obtained by the diffusion method used in the above experiments.

We now come to the second and, perhaps, more important feature of the curves shown in fig. 2, viz. the influence of temperature on the rate of volatilisation. The problem bears a close similarity to that of the emission of ions from a hot metal. Thus if we assume that the volatilised particles behave like a perfect gas, the calculation of the rate of volatilisation is analogous in practically all respects to that in the case just mentioned. Regarding the steady state as the result of a dynamical equilibrium between the molecules going from the layer of active deposit to the air and those going from the air to the deposit, we obtain the well-known relation connecting the rate with the absolute temperature T

$$\text{Rate} = \mathrm{AT}^{\frac{1}{2}}e^{-\mathrm{B}/\mathrm{T}}, \qquad (1)$$

where A and B are constants which can be determined experimentally.

The expression for the rate, just given, was first deduced by Richardson in his researches on emission of ions from hot bodies, and was subject to the condition that the number of free electrons per unit volume of the metal is independent of the temperature. He has since modified his views* by assuming that the number of free electrons in the metal is proportional to $\mathrm{T}^{\frac{3}{2}}$, whence

$$\text{Rate} = \mathrm{AT}^2e^{-\mathrm{B}/\mathrm{T}}. \qquad (2)$$

The assumption just mentioned was made in order to explain the observed values of the specific heat of electricity. More recently Richardson† has given another deduction of the second formula based on the quantum theory.

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* Richardson, 'Phil. Mag.,' vol. 23, p. 604 (1912).

† Richardson, 'Phil. Mag.,' vol. 28, p. 633 (1914).

Planck* also has obtained the relation $AT^2e^{-B/T}$ by consideration of the vapour pressure of a solid at very low temperatures, using the assumption that the entropy of the solid at these temperature will be practically independent of the temperature, while that of the vapour can be considered like that of a perfect gas.

It seems very doubtful, however, whether the assumptions used by Planck will apply to the case under consideration, *i.e.* to the evaporation of a metal at high temperatures. In this case, a lower power of the factor T would be expected.

Both the relations just given require that the rate should be constant when the temperature is constant, but, as we have already seen, this is far from being the case, the rate varying considerably with the amount of material volatilised.

Consequently we must introduce a factor $\phi(N)$ into the expression for the rate, in order to make this quantity in agreement with observations—the function $\phi(N)$ expressing the rate as a function of the number N of thorium B molecules volatilised. We now have

$$\text{Rate} = AT^n e^{-B/T}\phi(N), \tag{3}$$

where $n = \frac{1}{2}$ or 2.

The form of the function $\phi(N)$ has already been discussed from the physical standpoint, hence we need only concern ourselves with a consideration of the remaining factor. From observations of the initial rate of volatilisation at two different temperatures the values of A and B in equation (2) can be calculated, and the rates at any other temperatures deduced. The following Table provides a comparison between the observed and calculated values of the initial rates at different temperatures.

Absolute temperature T.	Observed rate.	Calculated rate, using relation $AT^{\frac{1}{2}}e^{-B/T}$.	Calculated rate from $AT^2e^{-B/T}$.
803	<0·01	Extremely small	Extremely small
998	0·5	0·53	0·59
*1031	1·4	1·4	1·4
1063	3·4	3·61	3·4
*1103	8·0	8·0	8·0
1133	20	23·5	16
1303	Very great	980	380

* The observed rates at these temperatures were used in the calculation of the constants A and B in the expressions for the rate.

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* Max Planck, "Die gegenwärtige Bedeutung der Quantenhypothese für die kinetische Gastheorie," 'Vorträge über die kinetische Theorie der Materie und der Electricität — Mathematische Vorlesungen an der Universität Göttingen,' VI.

Considering the extreme sensibility of the expressions $AT^{\frac{1}{2}}e^{-B/T}$ and $AT^2e^{-B/T}$ to small changes of temperature, the agreement between observed and calculated values is good. It will be noticed, however, that the factor $T^{\frac{1}{2}}$ or T^2 has practically no effect on the value of the expression for the rate until the temperature reaches a high value—thus both expressions for the initial rate of volatilisation agree equally well. It is only possible, experimentally, to distinguish between the two forms when the temperature is in the neighbourhood of 1000° C.; unfortunately at this temperature it is practically impossible to measure the initial rate. Similar results are found if, instead of using the initial rates, we consider the rates of volatilisation at a later stage of the process. Thus the rates of volatilisation at different temperatures when 40 per cent. of the active material has been removed are in the same relative proportion as the initial rates at the same temperatures. This only holds, however, up to a point where about 80 or 90 per cent. of the thorium B is volatilised. Beyond this point, the whole process is changed on account of the effects previously discussed.

The results of the experiments on the rate of volatilisation of the active deposit thus seem to support the view that the volatilisation proceeds on similar lines to the emission of ions (positive or negative) from a heated metal. Other experimenters have shown* that there is a close similarity between the laws of disintegration of a heated wire and the leak of positive electricity from it. The present experiments support this view, although the only safe conclusion which can be given at present is that the formula for the volatilisation—besides containing terms varying more slowly—may be expected to contain the factor $e^{-B/T}$ or $e^{-Q/RT}$, where R is the gas constant and Q the latent heat of vaporisation: this result, of course, is well known from ordinary thermodynamical considerations.

4. *Variation of the Temperature.*—From the point of view of interest this factor should have been considered earlier, but for several reasons it seemed advisable to defer it until the questions raised in Section 3 had been discussed. Barratt and Wood (*loc. cit.*) investigated the question by heating thorium active deposit for a constant time (15 minutes) at various accurately measured temperatures. Their work led to a result 750° C. as the temperature of volatilisation of thorium B. In the present experiments the procedure adopted was exactly the same—the constant period of heating in this case again being 15 minutes.

Curve A, fig. 4, is a combination of the results obtained in the present work with those obtained in a previous research by Barratt and the author. The observations made in the present research are indicated in the figure by a circle—those in previous work by Barratt and Wood by a combination of a circle and a cross. It will be seen that the two sets of observations are in excellent agreement. One important difference, however, should be noted.

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* See J. J. Thomson's 'Conduction of Electricity through Gases,' p. 213, Chap. VIII.

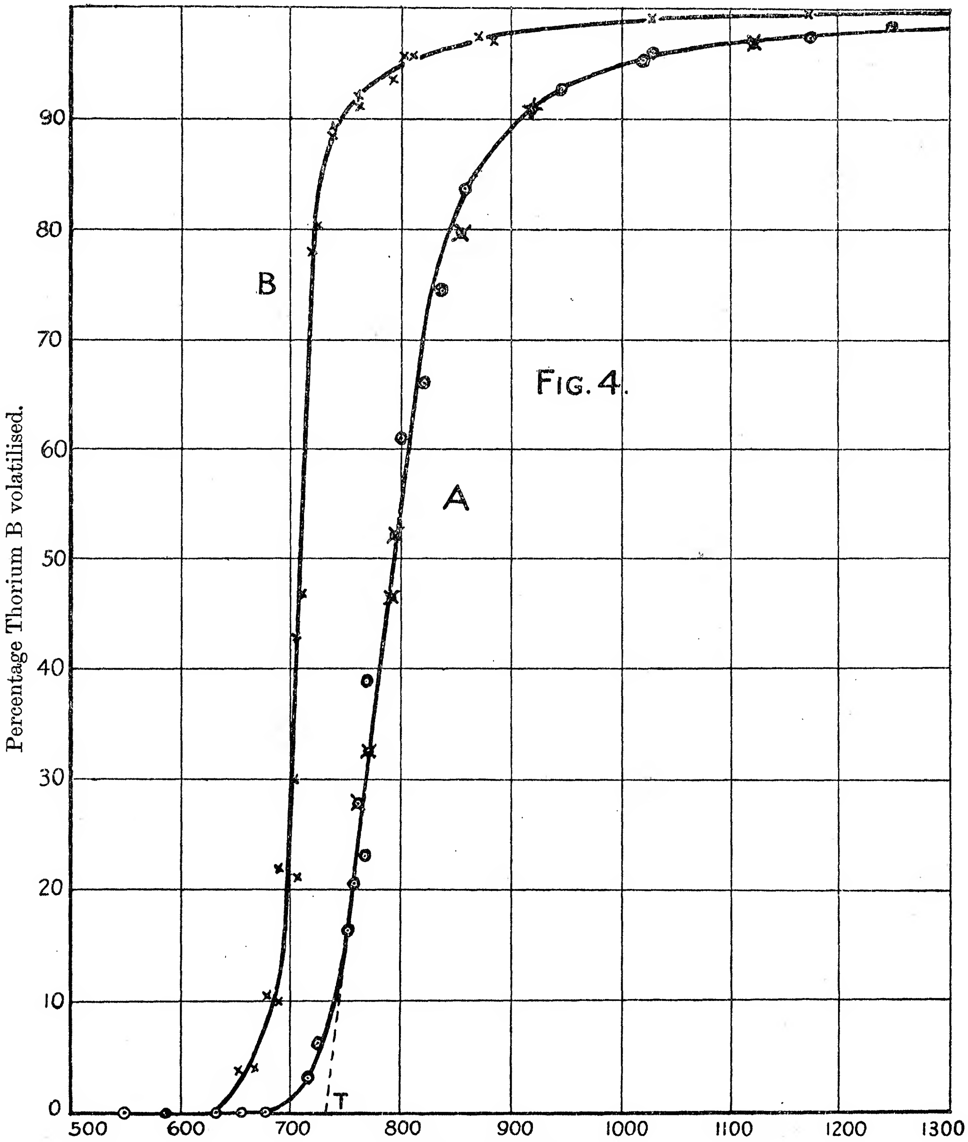

FIG. 4.

Temperature (degrees C.).
Curve A. At 760 mm. pressure.
Curve B. At 3 mm. pressure.
× × × ⊙⊙⊙ Present paper.
⊗ ⊗ ⊗ Barratt and Wood.

The temperature of volatilisation, as given by Barratt and Wood, was "slightly lower than 750° C."—it is evident from the figure that if the main portion of the curve is produced to cut the axis at T, the temperature obtained, 740° C., agrees very well with the value just given. This temperature, 740° C., is that at which the thorium B begins to volatilise very rapidly. Below this temperature, however, a small amount of volatilisation is observed, but this quickly falls to a quantity too small for detection at about 680° C. Of course, the lowest temperature at which it is possible to detect volatilisation is even lower than this, but in that case the time of heating must be considerably increased. The following observations at temperatures below 680° will illustrate this point:—

Temperature.	Percentage thorium B volatilised on heating.		
	(1) 15 minutes.	(2) 60 minutes.	(3) 5 hours.
° C.			
630	0	1	3
550	0	0	1

The form of the curve A, fig. 4, is interesting. It will be noticed that the amount volatilised increases at first slowly, then much more rapidly as the temperature increases. When a fairly large percentage has been removed, however, the rate of volatilisation rapidly falls off with further heating at higher temperatures. Of course, a series of curves similar to the one just described could be constructed from fig. 2 directly.

If the form of the function $\phi(\mathrm{N})$ in equation (3), Section 3, were accurately known it would be possible to calculate the total amount volatilised in a given time at any desired temperature.

5. *Variation of Pressure of the Surrounding Gas.*—All the experiments described up to this stage have been carried out with the air at atmospheric pressure in the silica tube. We shall now consider the effects observed when the active deposit was heated at pressures considerably lower than this. After its α-activity had been measured the active deposit on the platinum foil was placed on the nickel spoon and introduced into the silica tube. The air in the tube was immediately expanded into a bottle of large volume previously exhausted to the required pressure. Hence it was possible to obtain almost instantaneously any desired pressure in the tube by arranging that the volume of the receiver was very large compared with the volume of the silica tube. A series of observations of this kind, keeping

the time of heating constant (15 minutes), was made at different temperatures and pressures.

The result of such a series of observations at a pressure of 3 mm. is shown in curve B, fig. 4. Comparing the two curves A and B it is evident that the process of volatilisation takes place on very much the same lines in each case. Thus the slow initial rise, followed by the much steeper portion and ended by another slow increase, is characteristic of both curves. In the "low pressure" curve, however, the central portion is considerably steeper than the corresponding portion of the "atmospheric pressure" curve, indicating that volatilisation is much more rapid in the former case. Another difference between the two curves is the lowering (about 50° C.) of the initial temperature of volatilisation at low pressures. It should be noticed, too, that at low pressures it is still found practically impossible to volatilise the last traces of the active deposit.

The following Table gives a few of the results of a series of experiments carried out on the variation of the amount volatilised at different temperatures, the pressures varying from 760 mm. to 3 mm. of mercury:—

Temperature.	Percentage volatilised.			
	Pressure, cm. of mercury.			
	76 app.	15.	1·5.	0·3.
°C.				
710	4	18	60	67
757	18	47	83	92
800	45	73	93	96
1030	95	—	98·5	99
1175	97	—	—	99

Summary.

The more important factors which influence the volatilisation of extremely thin films of the radioactive deposits have been investigated experimentally. Each of these sources of influence has been considered separately by eliminating, as far as possible, the disturbing effects of the others. Thorium B, for reasons given in the earlier part of the paper, has been chosen as typical of all similar constituents of the active deposits of radium, thorium, and actinium.

The influence of the following factors on the process of volatilisation has been examined:—

(1) The surface on which the active substance is deposited.

(2) Variation of the "amount per square centimetre" of the active deposit collected on the surface.

(3) Variation of the period of heating. Curves connecting "percentage volatilised" with "time of heating" at a series of different temperatures are given.

(4) Variation of temperature—the time of heating remaining constant.

(5) Variation of the pressure of the surrounding gas.

It has been shown to be extremely difficult to remove, by heating alone, the last traces of the active deposit from surfaces of quartz, nickel, or platinum. A suggested explanation of this is given and verified experimentally. The most consistent results are obtained when the surface is exposed to the emanation without electric field, in which case the volatilisation is independent of the time of exposure to the emanation. The volatilisation is shown to obey practically the same law as the rate of emission of positive ions from a hot body, this expression—Rate $= AT^{n}e^{-B/T}$—being modified by the introduction of a factor $\phi(N)$ which depends on the amount of active deposit which has been volatilised. The function $\phi(N)$ is considered from a physical standpoint, the mathematical relation being extremely complex.

A comparison of the volatilisation curves at pressures of 760 mm. and 3 mm. is given, a lowering of the initial temperature of volatilisation at low pressure being observed. The volatilisation curve at atmospheric pressure agrees extremely well with that given in a previous paper by Barratt and Wood (*loc. cit.*).

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